

Outdoor infiltration and indoor contribution of UFP and BC, OC, secondary inorganic ions and metals in PM_{2.5} in schools

I. Rivas^{a, b, d, e, f, *}, M. Viana^a, T. Moreno^a, L. Bouso^{b, d, e}, M. Pandolfi^a,
M. Alvarez-Pedrerol^{b, d, e}, J. Fornes^{b, d, e, g}, A. Alastuey^a, J. Sunyer^{b, c, d, e}, X. Querol^a

^a Institute for Environmental Assessment and Water Research (IDEA-CSIC), C/ Jordi Girona 18-26, 08034 Barcelona, Spain

^b Centre for Research in Environmental Epidemiology (CREAL), C/ Dr. Aiguader 88, 08003 Barcelona, Spain

^c Hospital del Mar Research Institute (IMIM), C/ Dr. Aiguader 88, 08003 Barcelona, Spain

^d Universitat Pompeu Fabra (UPF), C/ Dr. Aiguader 88, 08003 Barcelona, Spain

^e CIBER Epidemiología y Salud Pública (CIBERESP), C/ Monforte de Lemos 3-5, 28029 Madrid, Spain

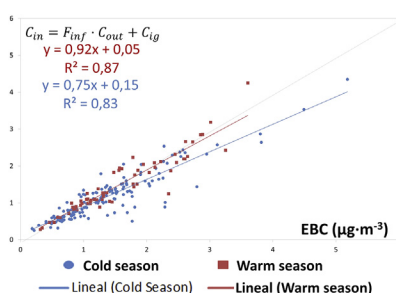
^f Institut de Ciència i Tecnologia Ambientals, Universitat Autònoma de Barcelona (UAB), Edifici C Campus UAB, 08193 Bellaterra Cerdanyola, Spain

^g Department of Genes and Environment, Division of Epidemiology, Norwegian Institute of Public Health, Oslo, Norway

HIGHLIGHTS

- Infiltration of outdoor pollutants into indoor air at schools is assessed.
- Many pollutants have a high infiltration, with maximum reached by EBC and Cd.
- Building age & type of window do not determine infiltration levels.
- Type of window and sandy playground determine indoor mineral levels.

GRAPHICAL ABSTRACT



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ABSTRACT

Infiltration of outdoor-sourced particles into indoor environments in 39 schools in Barcelona was assessed during school hours. Tracers of road traffic emissions (NO₂, Equivalent Black Carbon (EBC), Ultrafine Particles (UFP), Sb), secondary inorganic aerosols (SO₄²⁻, NO₃⁻, NH₄⁺) and a number of PM_{2.5} trace elements showed median indoor/outdoor (I/O) ratios ≤ 1, indicating that outdoor sources importantly contributed to indoor concentrations. Conversely, OC and mineral components had I/O ratios > 1. Different infiltration factors were found for traffic and secondary components (0.31–0.75 and 0.50–0.92, cold and warm season respectively), with maxima corresponding to EBC and Cd. Higher concentrations of indoor-generated particles were observed when closed windows hindered dispersion (cold season). Building age was not a major determinant of indoor levels. Neither were the window's material, except for NO₂ (with an increase of 8 µg m⁻³ for wood framed windows) and the mineral components (also dependent on the presence of sand in a distance <20 m) that reach the indoor environment via soil adhering to footwear with their dispersion being more barred by Aluminium/PVC framed windows than the wooden ones. Enlarged indoor concentrations of some trace elements suggest the presence of indoor sources that should be further investigated in order to achieve a healthier school indoor environment.

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* Corresponding author. Institute for Environmental Assessment and Water Research (IDEA-CSIC), C/ Jordi Girona 18-26, 08034 Barcelona, Spain.

E-mail address: irivas@creal.cat (I. Rivas).

1. Introduction

Since children spend most of their daily time in the indoor environment (around 90%, US-EPA, 2009), indoor air quality must be assessed when calculating child exposure to air pollutants; especially in schools where they spend around 30% of their weekdays (Fromme et al., 2007). Besides, it is important to determine the fraction of outdoor particles that enters the indoor environment and which factors affect this parameter. As a result, there is an increasing interest in this field (El Orch et al., 2014; MacNeill et al., 2012).

Outdoor air pollutants may intrude indoors by two main mechanisms (Chen and Zhao, 2011): through opened windows or doors (natural ventilation) and by infiltration through cracks and leaks in the building envelope (the latter being uncontrolled and having a relatively low exchange rate).

Different parameters may be used to assess the relationship between indoor and outdoor atmospheric particulate matter (PM) concentrations, such as the Indoor-to-Outdoor concentration (I/O) ratio and the Infiltration Factor (F_{inf} , Chen and Zhao, 2011).

The I/O ratio is an extensively used value of the relationship between indoor and outdoor PM concentrations (Abt et al., 2000; Arhami et al., 2010; among many others). However, since it is affected by many factors (mainly indoor particle sources, particle penetration and deposition rate), it is not always useful for understanding indoor–outdoor PM relationships. This might be the reason for inconsistencies among different studies (see Chen and Zhao, 2011). Notwithstanding, if measured for suitably long periods when no particles are generated indoors, the I/O ratio equals the F_{inf} (Long et al., 2001).

The F_{inf} represents the equilibrium of ambient PM that penetrates indoors and remains suspended, avoiding the influence of indoor-sourced PM. In natural ventilated buildings, this can be linearly expressed as (Dockery and Spengler, 1981):

$$C_{in} = F_{inf} \cdot C_{out} + C_{ig} \quad (1)$$

where C_{in} and C_{out} are the indoor and outdoor particle concentrations, respectively, F_{inf} is the infiltration factor and C_{ig} is the average concentration of indoor generated particles.

Outdoor PM may also reach indoor environments via soil adhering to footwear and clothes, and then be resuspended into the indoor air (Layton and Beamer, 2009) with this mechanism being favoured in highly crowded indoor environments, such as schools. Moreover, other processes such as phase change processes (e.g. volatilization of nitrate aerosol; Sangiorgi et al., 2013; Viana et al., 2014), new particle formation (e.g. from the interaction of outdoor O_3 and Volatile Organic Compounds, VOCs; Weschler, 2011 and references therein), and coagulation can influence in some cases the extent to which outdoor particles affect indoor levels (Weschler and Shields, 1999).

In addition to the need for characterising infiltration, assessing actual indoor exposures should also take into account indoor-sourced pollutants, always present in real-world conditions. At school, children participate in a wide variety of activities (e.g. painting, write on the blackboard, dance, move chairs). This results in schools being a very complex microenvironment affected by many different air pollutants (both gaseous or particulate compounds).

The occupancy-associated PM can be an important contributor to PM levels indoors. Although it may originate from the human body itself (skin flakes, hair, and other organic emissions, Fromme et al., 2008; Pegas et al., 2012), higher contributions come from human activities (walking, moving papers, etc.) that resuspend PM previously deposited on indoor surfaces such as floor and furniture

(Qian et al., 2014, and references therein). Finally, VOCs are also an important aerosol component in indoor environments being emitted by cooking (Abdullahi et al., 2013 and references therein), building materials, furniture and home complements (Edwards et al., 2001; Uhde and Salthammer, 2007) and by terpene-based cleaning products (Edwards et al., 2001; Singer et al., 2006). VOCs react with ozone (O_3) and nitrogen oxides (NO_x) and lead to gas-phase formation of secondary organic aerosols (SOA, Wang and Waring, 2014; Weschler and Shields, 1999) which are a constituent of Organic Carbon (OC, Turpin and Lim, 2001).

Within the framework of the BREATHE Project, this work focuses in the study of, on one hand, the infiltration of outdoor-sourced particles into indoor school environments (testing the effects of building age and type of window), and, on the other hand, the assessment of the indoor contribution of specific PM components, aiming to achieve an in-depth assessment of indoor air quality in primary schools in Barcelona (Spain).

2. Materials and methods

2.1. Study description and sampling sites

Two one-week sampling campaigns (covering different seasons) were carried out from February 2012 until February 2013 in 36 schools in Barcelona (15,993 inhab·km⁻²) and 3 schools in the near Sant Cugat del Vallès (1761 inhab/km², IDESCAT, 2012), NE Spain (Fig. 1).

Simultaneous indoor (in a classroom with pupils 7–10 years old) and outdoor (in the playground) sampling was carried out concurrently in two schools per week.

School buildings presented a wide range of ages (constructed from 1894 to 2010, information from the Property Tax Account Number, Table S1). All the schools were naturally ventilated by opening and closing windows, which were either Aluminium/PVC or wood framed. The type of windows in each school was reported during the monitoring period. The effect of these three parameters (open/closed windows, building age and type of window) on infiltration rates was evaluated.

2.2. Sampling and analysis

Air pollutants at schools were monitored during four working days (Monday to Thursday) per campaign. PM_{2.5} samples were daily obtained during school hours (9–17 h local time) with a MCV high volume sampler (30 m³ h⁻¹) on Pallflex quartz fibre filters (150 mm) to obtain mass concentration and a complete chemical characterisation, resulting in a total of 553 8 h-daily samples (283 indoors, 270 outdoors). A 1/4 fraction of each filter was bulk acid digested (HNO₃:HF:HClO₄) for the determination of major elements (Al, Ca, Fe, K, Na, Mg) by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) and trace elements (Li, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Cd, Sn, Sb, Pb, among others) by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Water-soluble ions (SO_4^{2-} , NO_3^- and Cl^-) were determined in another 1/4 filter by ion chromatography (ICHPLC) and NH_4^+ by a selective electrode. A 1.5 cm² filter punch was used for OC and elemental carbon (EC) determination by a thermal-optical transmission technique with a Sunset Laboratory OCEC Analyser with the NIOSH temperature programme (Birch and Cary, 1996). Sampling and analytical procedures are reported in detail by Querol et al. (2001a) and Rivas et al. (2014).

Besides filter samples, 10-min real-time Ultrafine Particles (UFP) number concentration in the range of 10–700 nm, UFP size (DiSCmini, Matter Aerosol) and Black Carbon (BC, MicroAeth AE51, AethLabs) concentrations were monitored, as well as weekly-averaged (including nights) NO₂ concentrations using Gradko

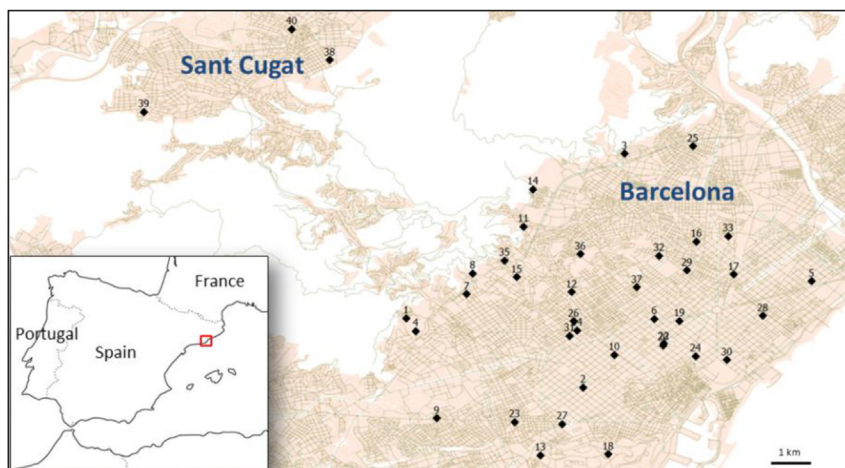


Fig. 1. Location of the schools across Barcelona and Sant Cugat.

Environmental passive dosimeters. All the DiSCmini devices were intercompared and corrected among each other to minimise measuring differences. BC concentrations recorded with the MicroAeth AE51 were converted to Equivalent Black Carbon (EBC) by means of a cross-correlation with in-situ (at schools) collected data of EC on filter samples.

2.3. Data treatment

I/O ratios (section 3.1.) and correlations (section 3.2) were calculated on individual daily basis (sample-by-sample) to avoid the dilution effect of the value when calculating the mean I/O ratio, except for NO₂ (weekly averaged). EBC and UFP real-time concentrations were also daily averaged, taking into account only school hours to coincide with filter data and to tighten the scope to infiltration processes occurring while children are in schools. In order to identify possible similar patterns, air pollutants have been grouped by common origin (some being in more than one group) including: road traffic tracers, components with a very high indoor-sourced fraction, minerals, secondary inorganic aerosols (SIA), marine aerosols, heavy oil combustion tracers, and industrial-sourced metals.

Schools monitored during periods with mean outdoor temperatures below 20 °C were classified into the cold season category and assumed to have the windows closed (59 cases; this is because 20 of the 39 schools were monitored twice, in both campaigns, under cold conditions); inversely, schools with temperatures above 20 °C were considered to be in the warm season and to have opened windows (17 cases). Fewer schools were monitored during the warm season because the longest holidays of the school year take place during summer (including the entire months of July and August). This classification was validated by a questionnaire about window opening filled in by the teachers during the sampling period.

A Linear Mixed-Effects Model (section 3.3.) was carried out with the software STATA 11 to assess the effect on indoor levels of building age, type of window and the presence of sand in the playgrounds. The equation that describes the model is:

$$Y_{it} = \beta_0 + \beta_1(\text{outdoorconcentration})_{it} + \beta_2(\text{typeofwindows: wood})_i + \beta_3(\text{building age: } \leq 1970)_i + \beta_4(\text{typeofplayground: sand - filled } < 20\text{m})_i + u_i + \varepsilon_{it} \quad (2)$$

where Y_{it} is the indoor concentrations for school i at day t ,

$t = \{1-8\}$, u_i are random effects at school level, assumed normally distributed with mean 0 and variance σ_u^2 , and ε_{it} are the model residuals assumed normally distributed with mean 0 and variance σ_ε^2 .

3. Results and discussion

3.1. Indoor/outdoor ratios and coefficients of variation

Descriptive statistics of the I/O ratios and their CV by season are presented in Fig. 2 (air pollutant concentrations are in Table S2). PM_{2.5} showed a median ratio above 1 (1.43 for the cold and 1.39 for the warm season), thus higher levels were found inside the classrooms than in the playground. This is due to important contributions of indoor sources to PM_{2.5} components, discussed in detail below. No significant differences can be observed between seasons.

Tracers of road traffic emissions in Barcelona (NO₂, EBC, UFP, Sn, Sb, Cu, Amato et al., 2009) had median I/O ratios below 1 during the cold season (higher levels outdoors), but very close to 1 for EBC, Cu and Sn. In a few schools Sn, Sb and Cu were an exception in the warm season when slightly higher median levels were found indoors, probably because of the synergies of opened windows and specific indoor emissions of these elements. UFP size median I/O ratio was also >1 since fresh exhaust emissions from traffic are very fine (20–30 as nm prevailing mode, Dall'Osto et al., 2011) but they increase their size by condensation and coagulation processes that might take place indoors. In fact, during the warm season the I/O UFP size ratio was approximately 1, with analogous processes affecting UFP due to similar conditions of temperature and humidity among both environments. In a number of schools, the I/O concentration ratios for EBC, UFP, Sb, Sn and Cu (Fig. 2) were >1, even in the cold season with closed windows. This occurs in schools where the monitored classroom was closer to traffic than the playground site (school characteristics in Table S1). Therefore, since some traffic tracers are very distance-dependent (Gilbert et al., 2003; Zhu et al., 2002), those schools were excluded in the analysis hereafter (16 of 76 cases; only for data of traffic related pollutants). In any case, this evidences the high infiltration rates for traffic related pollutants (MacNeill et al., 2012; Raysoni et al., 2011).

The indoor-sourced fraction of components such as OC (from organic and textile emissions from children and also related to indoor surface emissions), Ca and Sr (from chalk use in blackboards) is known to be higher than outdoor-sourced in schools, as observed in the currently schools under study by means of a PMF receptor model (Amato et al., 2014). The Organic/Textile/Chalk source (mainly explained by OC, Ca and Sr) contributed an average

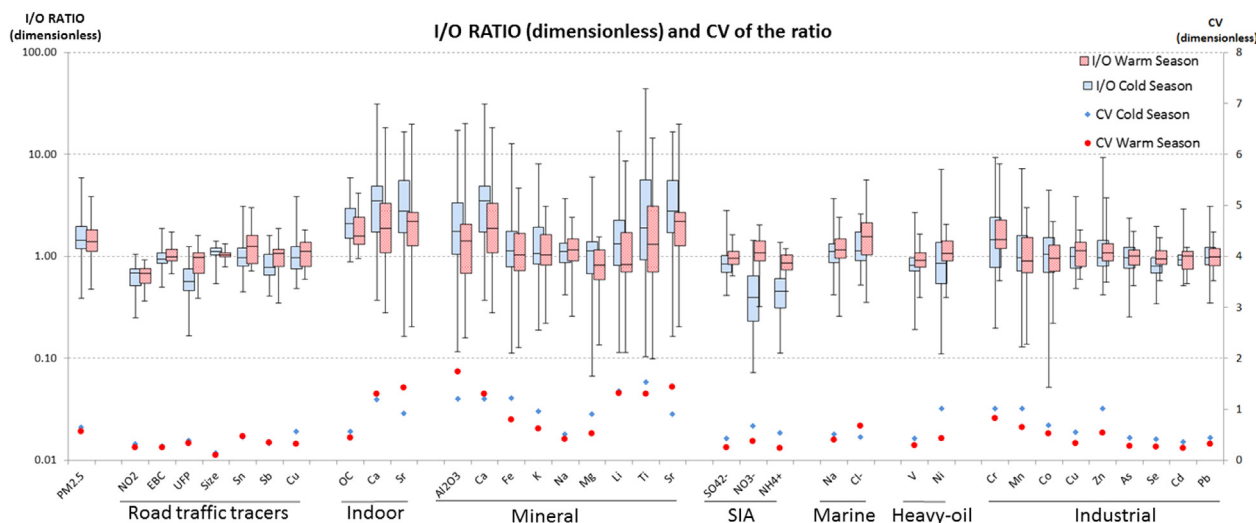


Fig. 2. Boxplot of the I/O ratio for PM_{2.5}, NO₂, BC, N, and PM_{2.5} components, main axis. CV of the I/O ratios, secondary axis. Concentrations below the detection limit have been discarded.

of 16.0 $\mu\text{g m}^{-3}$ to indoor levels whereas only 5.3 $\mu\text{g m}^{-3}$ were observed in the playgrounds. Consequently, I/O ratios for these specific PM_{2.5} components were greater than 1 in both seasons, especially during the cold period since the closed windows favour their accumulation. OC was particularly affected by indoor sources, since almost all its I/O ratio range was above 1. On the other hand, the range for I/O ratios was much wider for Ca and Sr because of varying intensities of chalk use and their mineral origin from sandy playgrounds.

Mineral components had the broadest range of I/O ratios, with a median ratio close to or higher than 1. Their levels were affected especially by the presence/absence of sandy playgrounds. The lowest I/O ratio for mineral elements was observed in schools with sandy playgrounds where outdoor samplers registered very high levels of mineral matter due to resuspension during children playground activities, and showing lower levels in classrooms (although they can also be considered high, since mineral particles were carried into the classroom by pupils; Layton and Beamer, 2009; Rivas et al., 2014). On the other hand, the maximum I/O ratios were found during the cold season because of the accumulation of indoor resuspended mineral particles and a lower resuspension in the playgrounds due to fewer outdoor activities during this colder period.

Regarding the SIA, the I/O ratios were clearly lower during the cold season, when median I/O values are below 1. This was especially evident in the case of NO₃⁻ (median I/O ratio: 0.39) and NH₄⁺ (median I/O ratio: 0.45), probably caused by the relatively high temperatures found indoors during the cold season, that led to a higher evaporation rate of the NH₄NO₃ (into HNO₃ + NH₃) and thus, a more important transition of the NO₃⁻ and NH₄⁺ from the PM to the gaseous phase (Harrison et al., 1994; Seinfeld and Pandis, 2006). During the warm season, I/O median values became very close to 1, due to windows opening and the fact that both indoor and outdoor temperatures were high enough to cause NH₄NO₃ evaporation (Querol et al., 2001b).

In spite of marine aerosols having an outdoor source, Na and Cl⁻ usually had higher levels indoors, especially during the warm season (Fig. 2). Probably because of Na also having a partial mineral origin in highly dusty environments (Amato et al., 2014; Viana et al., 2014) and Cl⁻ being emitted in indoor environments (by cleaning products, among others, Koistinen et al., 2004).

Focussing on trace elements, median I/O ratios for V and Ni

(mostly arising from shipping emissions in Barcelona, Amato et al., 2009) during the cold period were 0.82 for V and 0.86 for Ni, which increased to 0.91 and 1.07, respectively, during the warm season because the opened windows facilitated their entrance indoors. Regarding other trace metals related to industrial processes in Barcelona (Amato et al., 2009), we evidenced that Cr had clearly higher levels indoors in both seasons (I/O ratio = 1.46), with an indoor origin attributed to the abrasion of metallic components of chairs and tables (Cr is an important alloying element in stainless steel, with a minimum of 10.5 wt% required for the surface protective layer for corrosion prevention, Bettini, 2007). Moreover, Cr is also present as chromated copper arsenate (CCA), a preservative for furniture and wood building materials against insect, bacterial, and fungal decline (Patch et al., 2009). The rest of trace metals had median I/O ratios ~1, some with (a) a similar median I/O ratio during both periods: As and Pb; (b) others whose median I/O ratio was slightly higher during summer: Cu, Zn, Se and Cd, because of free entry through opened windows, and (c) those with slightly lower I/O ratio during summer: Mn and Co. In specific schools (6 of 39) both winter and summer I/O ratios were markedly high for elements such as Cr, Cu and As, this probably pointing to the above mentioned emissions from indoor materials or material-treatments that may be relevant for children exposure.

Based on these I/O ratios, both highly indoor-sourced components and mineral components were barred from the analyses in section 3.2 owing to important indoor sources of these components. Other elements might be partly indoor-sourced (Bruinen de Bruin et al., 2006), but outdoor sources were considered predominant and therefore NO₂, EBC, UFP, Sb, SO₄²⁻, NO₃⁻, NH₄⁺, V, Ni, Cr (although having high indoor contribution), Cu, As, Se and Pb, were included in the analyses in section 3.2.

Previous studies have reported I/O ratios at schools. Regarding PM_{2.5}, Zwoździak et al. (2013) obtained a mean I/O ratio of 2.0 during winter and 4.1 during summer in a school in Wrocław (Poland), and Stranger et al. (2008) of 1.3 and 2.3 during winter and summer respectively. During winter, our mean I/O ratio (1.86) is between those found by Zwoździak et al. (2013) and Stranger et al. (2008), but in summer they found mean I/O ratio much higher than ours (1.59). For UFP number concentrations, Diapouli et al. (2007) reported I/O ratios between 0.55 and 0.85 in seven primary schools in Athens (Greece), Mullen et al. (2011) between 0.48 and 0.77 in six schools in northern California (USA) and Buonanno et al.

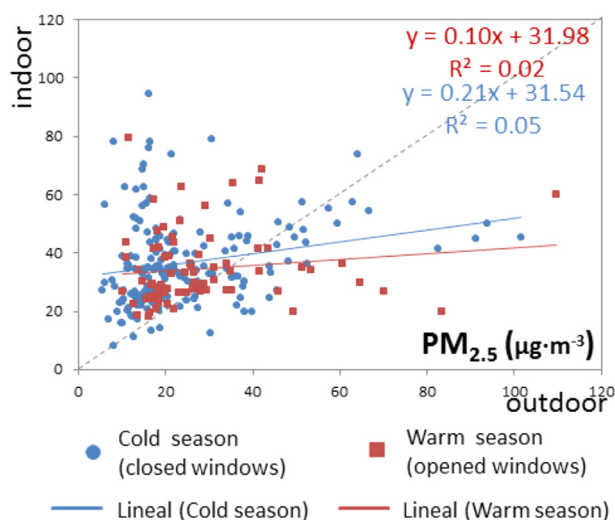


Fig. 3. Scatterplot showing the indoor–outdoor correlation for $PM_{2.5}$, distinguishing by ventilation variable (determined by window's configuration).

(2013) between 0.63 and 0.74 in three schools in Cassino (Italy), all of them during school hours. The median I/O value for UFP in our study (0.66) is within the range of the abovementioned studies; however our I/O range is clearly wider (from 0.17 to 1.62). Pegas et al. (2011) obtained an I/O ratio range for NO_2 of 0.36–0.95 in 14 schools in Lisbon (Portugal), similar to ours (0.25–1.05). Our mean I/O ratio for NO_2 is 0.65, the same that Stranger et al. (2008) found during winter (0.6) but lower to what they found during summer (1.2) in 27 schools in Antwerp (Belgium).

The CV is a normalised measure of dispersion corresponding to the ratio of the standard deviation to the mean and permits the comparison of data with very different means. CV of UFP number concentration was used to quantify spatial variation in microscale environments among 25 schools in Brisbane (Australia), 12 of them showing the presence of spatial variation of UFP (Salimi et al., 2013). In the present work, CV is used to analyse the variation on I/O ratios among schools (Fig. 2). Pollutants related to road traffic emissions had a very low CV (below 0.50, except Cu during the cold season whose CV = 0.55) as well as the SIA (except NO_3^- during the cold season, due to evaporation) and some trace metals (As, Se, Cd and Pb). This indicates that the indoor-to-outdoor relationship of these pollutants was quite similar for all schools and seasons (especially those sourced by traffic). For SIA and trace elements (except Ni and Cd), lower CVs were found during the warm season, probably related to the windows being opened and their free entrance independently of windows and building leaks.

On the other hand, mineral components had CV close to or above 1, with a high variability of the I/O ratio among the schools, especially during the cold season. This might be derived from two causes: (1) the presence/absence of sand playgrounds that specially affect outdoor levels and can make the I/O ratio to strongly diminish, and (2) indoor levels being influenced by the number of pupils and by their activity intensity, resulting in a wide range of I/O ratios.

General trends can be summarised in OC, Ca, Sr, Na, Cl^- and many mineral components (Al_2O_3 , Li, Ti, Fe) having I/O ratios >1 and more markedly during the cold season, because of their accumulation indoors due to the closed windows. On the other hand, traffic tracers (NO_2 , EBC, UFP, Sn, Sb, Cu), SO_4^{2-} and the trace elements Ni and V were characterised by having I/O ratios <1 (more pronounced during the cold season), because of their source being

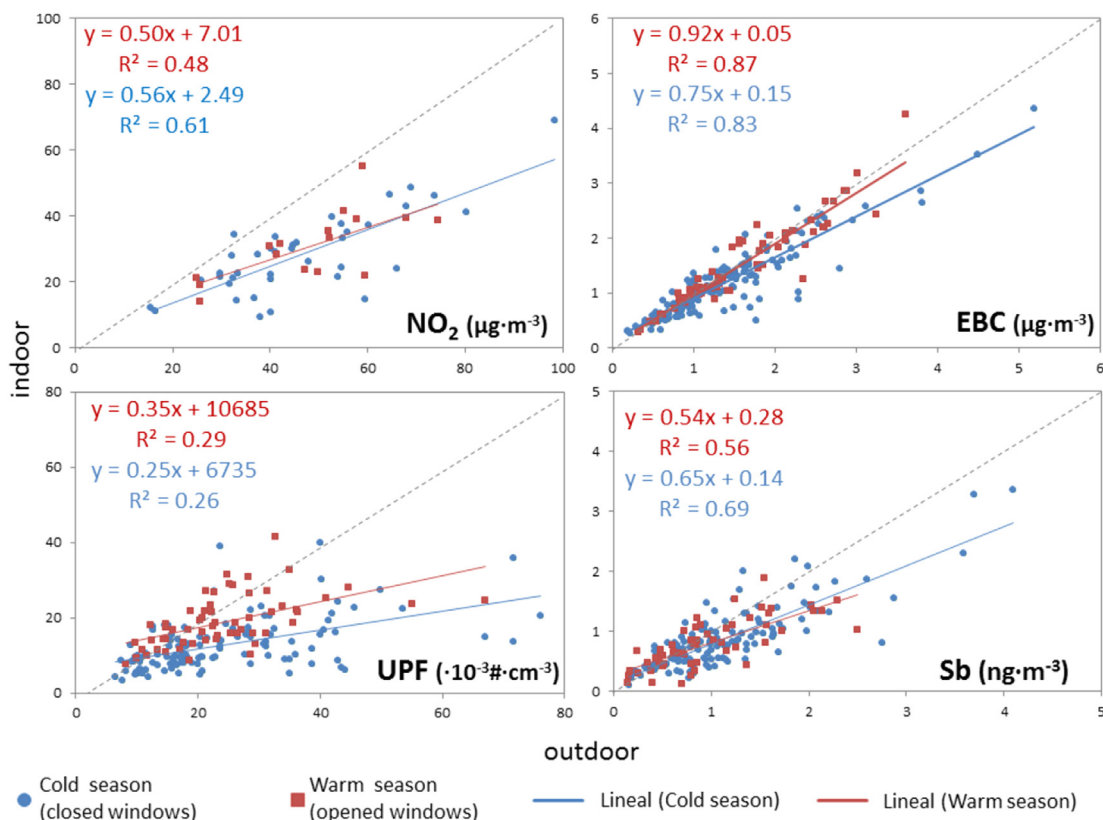


Fig. 4. Scatterplots showing indoor–outdoor correlations for selected traffic-related pollutants, distinguishing by ventilation variable (determined by window's configuration). Some schools have been excluded due to monitored classroom being closer to street than playground (see text for details).

located outdoors. UFP size, as well as some mineral elements (K, Mg), have I/O ratios close to 1.

3.2. Infiltration factors and indoor generated particle concentrations

The effect of windows opening on the F_{inf} and C_{ig} was evaluated (windows were closed during the cold season and opened during the warm one). Indoor versus outdoor daily levels (weekly levels for NO_2) for different air pollutants are presented in Figs. 3 and 4 and S1–S7. Linear regression lines correspond to Eq (1), and, therefore, the slope stands for the F_{inf} , and the intercept for the C_{ig} . A similar assessment was carried out by Sangiorgi et al. (2013) in 4 offices in Milan.

The indoor–outdoor correlation for $PM_{2.5}$ (Fig. 3) shows a zero coefficient of determination (R^2) for both warm and cold season. The flat slopes (0.10 for the warm and 0.21 for the cold season) are due to the very high intercepts obtained (31.98 for the warm and 31.54 for the cold season). These intercepts indicate a very high contribution of indoor sources to $PM_{2.5}$ and when important indoor sources are present, the slope does not correspond to the F_{inf} . This is the reason why in the previous section those components with significant indoor sources were excluded from this analysis (although they are presented in italics in Table S3 and some

scatterplots are shown as examples in Fig. S1). These components have an $R^2 < 0.3$ (Table S3), which can be regarded as the lowest threshold to consider the F_{inf} as a reasonable one.

Schools having I/O ratios above 1.2 for traffic-sourced pollutants (generally because of the classroom being closer to the street than the playground) were not considered for the analysis of the components related to traffic owing to their distance-dependence stated previously. NO_2 showed a higher R^2 during the cold season ($R^2_c = 0.61$) than during the warm one ($R^2_w = 0.48$), but similar F_{inf} for both seasons ($F_{inf,c} = 0.56$ and $F_{inf,w} = 0.50$, cold and warm respectively) indicating similar infiltration independently of the windows opening (Fig. 4). Even for schools with classrooms closer to the street than the playground (not included in the correlation), the I/O ratios were below 1. This might be explained by the indoor consumption of NO_2 in gas-phase reactions with terpenes and other unsaturated hydrocarbons (Uhde and Salthammer, 2007; Weschler and Shields, 1999).

In the case of EBC (Fig. 4), very good correlations were found in both seasons ($R^2_w = 0.87$; $R^2_c = 0.83$). Based on the F_{inf} , 92% of indoor EBC comes from outside during the warm season and 75% during the cold one, being the second pollutant with the highest F_{inf} in the cold season (after Cd) and the first in the warm period. This indicates that closing the windows scarcely prevent the infiltration of outdoor EBC particles. For Sb, high R^2 were also found ($R^2_w = 0.56$ and $R^2_c = 0.69$), but the F_{inf} was lower than for EBC ($F_{inf,w} = 0.54$; $F_{inf,c} = 0.65$). NO_2 , EBC and Sb have very low intercepts, indicating the absence of significant indoor sources for these pollutants.

Low correlation and F_{inf} for UFP ($F_{inf,w} = 0.35$, $R^2_w = 0.29$; $F_{inf,c} = 0.25$, $R^2_c = 0.26$) were found (Fig. 4), because of indoor particle sources ($C_{ig,w} = 10,685$ and $C_{ig,c} = 6,735$) that might increase indoor UFP independently of outdoor particles (Reche et al., 2014), and because of coagulation and condensation processes that might affect UFP indoors. In fact, Kearney et al. (2011) found that in 65% of the homes they studied, the indoor-generated UFP were higher than the UFP that infiltrated from outdoors. Actually, schools in Barcelona had higher indoor particle number concentrations during warm season despite the lower levels found outdoors during the same period (Fig. 4, Table S2). This might not only be explained by opened windows but also by the interactions of infiltrated outdoor O_3 with surfaces and household products that may generate new particles in the UFP range (Weschler, 2011). Further research is necessary in this field.

As regard for the infiltration of SIA (Fig. S2), we can observe very different patterns. Infiltration was high for SO_4^{2-} , with outdoor sources contributing 79% ($R^2_w = 0.85$) during the period with opened windows and 71% ($R^2_c = 0.77$) during the cold season. We are not aware of major indoor sources of fine SO_4^{2-} (in fact, C_{ig} is very low in both seasons) and thus this PM component is often used for the determination of infiltration rates as it can be considered a relatively inert tracer (Harrison et al., 1994). NO_3^- and NH_4^+ had a similar behaviour during the cold season ($F_{inf,c} = 0.31$, $R^2_c = 0.66$ for NO_3^- ; $F_{inf,c} = 0.41$, $R^2_c = 0.69$ for SO_4^{2-}) since the most common NO_3^- bearing species in PM is NH_4NO_3 (Seinfeld and Pandis, 2006). These low F_{inf} are affected by two conditions: the barrier from building shell and windows, but also the evaporation of NH_4NO_3 indoors. Similar results were obtained in offices in Milan (Sangiorgi et al., 2013). Very low concentrations of NO_3^- during the warm season led to a low $R^2_w = 0.36$. On the other hand, since NH_4^+ can also combine with SO_4^{2-} , (Ottley and Harrison, 1992) a $F_{inf,w} = 0.86$ ($R^2_w = 0.88$) is obtained, similarly to SO_4^{2-} .

Contrary to expectations, for some specific trace elements and in certain schools, higher levels were detected indoors than outdoors, what means that important indoor sources were present for these PM components. Among trace metals, V and Cd had the highest F_{inf} ($F_{inf,c} = 0.71$ and $F_{inf,w} = 0.75$ for V; $F_{inf,c} = 0.79$ and $F_{inf,w} = 0.70$ for

Table 1

Adjusted infiltration factor (F_{inf}), adjusted concentration of indoor generated particles (C_{ig}) and fraction of C_{ig} from the median indoor concentration of each component (C_{ig} intensity) after adjusting by type of windows, building age and presence of sand in playgrounds (cold season only). In bold, $F_{inf} > 0.5$ and C_{ig} intensities $> 50\%$.

| | F_{inf} | C_{ig} | C_{ig} intensity |
|------------------|---------------|---------------------|--------------------------------|
| | | ($pt\ cm^{-3}$) | (% indoor median) ⁺ |
| UFP [‡] | 0.25** | 8692** | 73.7 |
| | | ($\mu g\ m^{-3}$) | |
| $PM_{2.5}$ | 0.31** | 33.46** | 97.1 |
| NO_2 | 0.46** | 2.12 | 7.6 |
| EBC [‡] | 0.77** | 0.19** | 18.7 |
| SO_4^{2-} | 0.70** | 0.19* | 26.5 |
| NO_3^- | 0.31** | −0.06 | −13.3 |
| NH_4^+ | 0.41** | 0.03 | 10.0 |
| OC | 0.43** | 8.93** | 90.0 |
| Ca | −0.07 | 2.24** | 150.8 |
| Sr | 0.06 | 5.37** | 117.9 |
| Al_2O_3 | 0.17** | 1.42** | 168.4 |
| Fe | 0.09** | 0.50** | 163.4 |
| K | 0.23** | 0.39** | 120.7 |
| Na | 0.50** | 0.19** | 75.4 |
| Cl^- | 0.55** | 0.36** | 59.2 |
| Mg | 0.13** | 0.19** | 156.5 |
| | | ($ng\ m^{-3}$) | |
| Li | 0.05** | 0.74** | 203.6 |
| Ti | 0.08 | 64.88** | 151.2 |
| Sb [‡] | 0.65** | 0.23** | 30.3 |
| V | 0.72** | 0.58** | 23.6 |
| Ni | 0.52** | 0.82* | 42.9 |
| Cr | 0.38** | 4.76** | 138.6 |
| Mn | 0.14** | 13.37** | 148.9 |
| Co | 0.19* | 0.26** | 174.7 |
| Cu^{2+} | 0.43** | 4.41** | 61.2 |
| Sn^{2+} | 0.59** | 0.95** | 44.3 |
| Zn | 0.63** | 24.41** | 54.7 |
| As | 0.56** | 0.21** | 55.7 |
| Se | 0.46** | 0.15** | 61.9 |
| Cd | 0.81** | 0.02 | 13.3 |
| Pb | 0.57** | 2.93** | 46.7 |

[‡] Schools having I/O ratios above 1.2 for traffic-related pollutants have not been considered.

* Statistically significant at p-value ≤ 0.05 .

** Statistically significant at p-value ≤ 0.01 .

⁺ Median of the indoor concentrations during the cold period.

Table 2

Coefficients (difference in concentration) and fraction of the coefficient from the median indoor concentration for building age, type of windows, and type of playgrounds, after adjusting for outdoor concentrations (cold season only).

| | Building construction year: ≤ 1970 (Ref: > 1970) | | Type of window: Wood (Ref: Al/PVC) | | Playground: Sand-filled < 20 m (Ref: Paved/Sand > 20 m) | |
|--------------------------------|---|------------------------------|--------------------------------------|------------------------------|--|------------------------------|
| | Coeff | % Indoor median ⁺ | Coeff | % Indoor median ⁺ | Coeff | % Indoor median ⁺ |
| UFP ^a | (pt cm ⁻³) -2366 | -20.1 | (pt cm ⁻³) -2781 | -23.6 | (pt cm ⁻³) 954 | 8.09 |
| PM _{2.5} | ($\mu\text{g m}^{-3}$) -2.30 | 103.63 | ($\mu\text{g m}^{-3}$) -10.75** | -31.20 | ($\mu\text{g m}^{-3}$) 8.89** | 25.81 |
| NO ₂ | 2.55 | 9.12 | 8.06** | 28.78 | 0.69 | 2.47 |
| EBC ^a | -0.07 | -7.10 | -0.14 | -13.21 | 0.11 | 11.11 |
| SO ₄ ²⁻ | -0.10 | -13.56 | -0.05 | -6.57 | -0.05 | -6.64 |
| NO ₃ ⁻ | 0.06 | 11.67 | 0.21 | 4.33 | -0.10 | -20.81 |
| NH ₄ ⁺ | -0.09 | -30.68 | 0.11 | 38.44 | -0.08 | -26.54 |
| OC | -0.01 | -0.08 | -2.25* | -22.65 | 1.23 | 12.38 |
| Ca | -0.21 | -13.94 | -1.01** | -68.12 | 0.67 | 44.89 |
| Sr | 0.12 | 2.71 | -1.80* | -39.48 | 1.08 | 23.63 |
| Al ₂ O ₃ | -0.46 | -54.63 | -0.70** | -82.79 | 1.07** | 127.78 |
| Fe | -0.15* | -49.30 | -0.23** | -72.12 | 0.41** | 133.56 |
| K | -0.09 | -28.06 | -0.17** | -53.11 | 0.39** | 120.73 |
| Na | -0.02 | -8.30 | -0.07** | -26.24 | 0.03 | 13.93 |
| Cl ⁻ | -0.05 | -8.36 | -0.07 | -11.66 | 0.17* | 28.20 |
| Mg | -0.04 | -30.57 | -0.07** | -58.41 | 0.10** | 84.84 |
| Li | (ng m ⁻³) -0.27* | -73.19 | (ng m ⁻³) -0.37* | -10.24 | (ng m ⁻³) 0.65** | 179.33 |
| Ti | -15.85 | -36.93 | -27.19* | -63.35 | 53.00** | 123.49 |
| Sb ^a | -0.15 | -19.63 | -0.08 | -10.34 | 0.22 | 28.52 |
| V | 0.01 | 0.36 | -0.68* | -27.63 | 1.04* | 41.96 |
| Ni | 0.02 | 0.85 | 0.06 | 2.91 | 0.12 | 6.01 |
| Cr | -1.95* | -56.94 | -1.25 | -36.28 | 0.87 | 25.49 |
| Mn | -3.93 | -43.75 | -6.25** | -69.59 | 10.10** | 112.41 |
| Co | -0.09* | -62.41 | -0.10* | -66.23 | 0.09 | 63.38 |
| Cu ^a | -0.10 | -1.33 | -0.66 | -9.15 | 0.00 | 0.03 |
| Sn ^a | -0.36 | -16.98 | 0.05 | 2.39 | -0.05 | -2.42 |
| Zn | -6.22 | -13.93 | -7.32 | -16.40 | 3.13 | 7.01 |
| As | -0.02 | -6.54 | -0.09* | -25.29 | 0.11* | 30.44 |
| Se | -0.05* | -18.99 | 0.02 | 6.61 | -0.03 | -12.84 |
| Cd | 0.01 | 4.79 | 0.01 | 4.84 | -0.02 | -15.60 |
| Pb | -0.16 | -2.57 | -0.86 | -13.73 | 1.18 | 18.75 |

^a Schools having I/O ratios above 1.2 for traffic-related pollutants have not been considered.

*Statistically significant at p-value ≤ 0.05 .

**Statistically significant at p-value ≤ 0.01 .

⁺Median of the indoor concentrations during the cold period.

Cd; Fig. S3) and lowest C_{ig} with respect to the median, (being the C_{ig} the 21.9 and 11.1% of the median for V; and 16.5 and 37.4% (the latter not being low) for Cd, cold and warm season respectively, Table S3). Pb had a similar F_{inf} ($F_{inf,c} = 0.55$ and $F_{inf,w} = 0.61$), but with higher R^2 , than the rest of trace metals (excluding mineral components). For Pb, C_{ig} represents 46% (cold) and 42% (warm) of the median indoor concentrations, also indicating the presence of indoor sources such as old lead-based paints (Clark et al., 1991). However, no differences can be observed when considering building age, as will be described in section 3.3, so there might be other indoor sources that importantly contribute to Pb.

Trace metals (except Sb and Cr) had lower F_{inf} during the cold season, thus the entrance of these elements was to some extent hindered by windows (Table S3). However, for Ni, As, Cu, and Se the R^2 are not very high (the highest being 0.49 for As during warm season) because the impact of indoor sources might differ in each school. In fact, the abovementioned, and especially Cr, were affected by significant indoor sources in a number of schools (Fig. S3, Table S3). The C_{ig} represents 47% and 42% of the Ni median concentration, 59% and 52% of Cu, 51% and 39% of As, and 52% and 31% of Se, cold and warm seasons respectively. Cr should be highlighted, with the intercept accounting for 95% and 83% of its median indoor concentrations (cold and warm seasons, respectively). Therefore, the F_{inf} of Cr should not be determined by this analysis.

Further research is required in order to identify indoor sources of these trace metals, some being well-known because of their toxicity. With the exception of Sb, all trace elements had similar or higher C_{ig} during the cold than the warm season, due to the dispersion of the indoor generated PM to outdoors being hindered by the closed windows.

In summary, for many components the F_{inf} was similar across warm and cold seasons (generally with a slightly higher infiltration during the warm season) with the exception of EBC, SO_4^{2-} and Se, which had significantly higher infiltration rates during the period when the windows were opened.

3.3. Effect of building age, type of windows and type of playground in the F_{inf} , C_{ig} and indoor concentrations

Building age might have an effect on infiltration, and consequently on indoor pollutant concentrations, since older buildings might have more cracks on the building shell due to deterioration or to less isolating building materials and techniques. Walls are responsible for 18–50% of the infiltration air leakage in a building, and windows and doors (when closed) for 6–22% (Dickerhoff et al., 1982; Harrje and Born, 1982). The type and features of the windows (aluminium or PVC (Al/PVC) vs wood framed windows in this study) may also play an important role on the air leakage of this

building component (Younes et al., 2011). Moreover, the presence/absence of sand-filled playgrounds at schools have an influence on both indoor and outdoor levels of mineral components.

In BREATHE schools, the type of window was not related to building age (Pearson $\chi^2 = 0.61$, $p = 0.43$; Table S4). Indeed, a higher proportion of Al/PVC framed windows was present in the older buildings (65%) than in the newer ones (53%), probably due to recent renovation works. We performed linear mixed-effects models (LMM) including school as random effects. Multilevel modelling takes into account the hierarchical structure of the present data (measures grouped within schools). Table 1 shows the adjusted F_{inf} (F'_{inf}) and C_{ig} (C'_{ig}) for the pollutants under study during the cold season (closed windows) obtained by LMM. Only the cold season has been studied in this section to avoid the effect of higher infiltration during the warm season due to opened windows and, thus, focus on the effect of type of windows and building age. Moreover, since the mineral components have also been evaluated with this model, the variable type of playground (sand presence at < 20 m) has also been included. The objective is to highlight that the effect of outdoor concentrations in indoor concentrations (and therefore, for those components which are outdoor sourced, their infiltration) is isolated from the effect of the type of window, building age and type of playground. Except for NO_2 , the F'_{inf} (Table 1) for the cold season has not substantially changed when compared to the non adjusted factors presented in the previous section (Table S3). As stated before, Cd and EBC are clearly the pollutants with the highest F'_{inf} (0.81 for Cd and 0.77 for EBC), followed by V, SO_4^{2-} , Sb, Zn, Sn, Pb, Cl^- , Ni, and Na, all of them with a $F'_{inf} > 0.50$.

The C'_{ig} was generally higher than the non-adjusted. The proportion of the median that the C'_{ig} represents is also shown in Table 1. From the pollutants assessed, those with the highest impact of C'_{ig} were (excluding mineral components, all of them with very high C'_{ig}): Cr > OC > Na > UFP > Se > Cu > Cl^- > As > Zn, all of them having >50% of the median indoor concentrations from indoor origin (in bold in Table 1).

Table 2 shows the coefficients for each of the pollutants of the categorical variables (2 categories) “Building Age”, “Type of windows” and “Playground”. The coefficient indicates the increase in concentration (in the corresponding units) in case of having an older building (constructed ≤ 1970) with respect to a newer one (constructed >1970; which is the reference format) for the “Building age” variable, a wood framed windows with respect to Al/PVC framed windows (“Type of windows” variable); and the presence of sand in the playgrounds at a distance <20 m (with respect to paved playgrounds or playgrounds with sands at >20 m, which is the reference state). Correlations by building age and type of windows are shown in the Supplementary material (Figs. S4–S7).

Results evidence that the age of the school building was significantly (p -value<0.05) associated with indoor levels for Fe and 4 trace elements, most of them typically related to industrial emissions (Table 2). Negative coefficients indicate that newer buildings tend to have around $0.15 \mu g m^{-3}$ more of Fe, $1.95 ng m^{-3}$ of Cr, $0.27 ng m^{-3}$ of Li, $0.09 ng m^{-3}$ of Co, and $0.05 ng m^{-3}$ of Se than the older ones, probably due to higher indoor emissions of these elements by new materials but further research is needed to identify specific sources in indoor environments. The lack of association with indoor levels for most of the pollutants under study is in accordance with previous studies (which included newly constructed schools) that did not find any correlation between airtightness and building age (Sherman and Chan, 2004). Moreover, the type of window seems to be importantly associated with higher levels of mineral components (such as Al_2O_3 , Fe, Mg) and the components with a very high contribution from indoor sources (OC, Ca, Sr) in those schools with Al/PVC windows. Mineral components

may reach indoor environments more importantly via soil adhering to footwear and clothes than by infiltration. Therefore, the presence of a more isolating window (such as the Al/PVC framed instead of wood framed) would be a much important barrier for the dispersion of mineral components, which might keep resuspended indoors in such a crowded environment. Moreover, also higher indoor levels of Co and As were found in schools with Al/PVC windows, probably due to indoor emissions or because of their possible presence on the school sand. On the other hand, NO_2 infiltration was hindered by Al/PVC windows, since those schools with wood framed windows tend to have an increase of around $8 \mu g m^{-3}$ of NO_2 . The presence of sand-filled playgrounds had an impact also on indoor concentrations. Schools with sandy playgrounds at <20 m showed a substantial increase of mineral components in indoor concentrations with respect to those with paved playgrounds or sand at >20 m.

4. Conclusions

Infiltration of outdoor-sourced particles into indoor school environments and the identification of indoor sources of PM (including metals) were assessed in 39 schools in Barcelona with the aim to evaluate the infiltration of outdoor-sourced particles into indoor school environments (testing the effects of building age and type of window in this process), and, on the other hand, the indoor contribution of specific PM components.

I/O ratios trends can be summarised in OC, Ca, Sr, Na, Cl^- and many mineral components (Al_2O_3 , Li, Ti, Fe) having I/O ratios >1 and more markedly during the cold season, because of their accumulation indoors due to the closed windows. On the other hand, traffic tracers (NO_2 , EBC, UFP, Sn, Sb, Cu), SO_4^{2-} and the trace elements Ni and V were characterised by having I/O ratios ≤ 1 (more pronounced during the cold season), because of their source being located outdoors.

Indoor-outdoor correlations permit to obtain the infiltration factor (F_{inf} , only when $R^2 > 0.3$) and the indoor-generated concentration (C_{ig}). For many components the F_{inf} was similar across warm and cold seasons (generally with a slightly higher infiltration during the warm season when windows are opened). Cd and EBC were clearly the pollutants with the highest F_{inf} in the cold season (0.81 for Cd and 0.77 for EBC), followed by V, SO_4^{2-} , Sb, Zn, Sn, Pb, Cl^- , Ni, and Na, all with a $F_{inf} > 0.50$. Some metals may have higher indoor levels in newer buildings (constructed after 1970) due to specific indoor materials or treatments. Window's frame material affects more importantly to mineral components, hindering their dispersion and leading to higher indoor concentration in schools with Al/PVC window (those mineral components easily reach the indoor environment by soil adhering to footwear). Moreover, higher indoor concentrations of mineral components in schools were related with the presence of sand-filled playgrounds.

Schools are characterised by having a crowded indoor environment where many different activities take place. These characteristics lead to a complex mixture of emissions of different air pollutants that should be characterised when dealing with exposure to indoor PM_{10} . The characterisation of specific indoor sources is a key topic that should be furthered investigated in order to achieve a healthier school indoor environment.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2015.01.055>.

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